Transport anomalies across the quantum limit in semimetallic $Bi_{0.96}Sb_{0.04}$

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We report on a study of electronic transport in semi-metallic $Bi_{0.96}Sb_{0.04}$. At zero field, the system is a very dilute Fermi liquid displaying a T^2 resistivity with an enhanced prefactor. Quantum oscillations in resistivity as well as in Hall, Nernst and Seebeck responses of the system are detectable and their period quantifies the shrinking of the Fermi surface with antimony doping. For a field along the trigonal axis, the quantum limit was found to occur at a field as low as 3T. An ultraquantum anomaly at twice this field was detected in both charge transport and Nernst response. Its origin appears to lie beyond the one-particle picture and linked to unidentified many-body effects.

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It has been known for a long time that doping elemental bismuth with antimony decreases the carrier density and eventually leads to a semimetal to semiconductor transition[1, 2]. Bi_xSb_{1-x} alloys are remarkable n-type thermoelectric material operating near 100 K[3]. The evolution of their Fermi surface [4], notably under pressure[5, 6], as well as their transport coefficients above 4.2 K[7] have been intensively studied. They are attracting new attention in the context of research on "topological insulator", which was first proposed [8] and then reported to be detected[9] in this family on the semiconductor side (i.e. for $x > 0.08$). The metallic side of this semimetallic-semiconductor phase boundary permits to explore the instabilities of an ambipolar three-dimensional electron gas as the carrier density is continuously pushed to zero[10]. Moreover, the small size of the Fermi surface pulls down the quantum limit. This limit is attained when all carriers are at the lowest Landau level. The barely-screened Coulomb repulsion of the semimetal at zero-field is expected to become even stronger beyond this limit. In the case of pure bismuth, the quantum limit is attained by a field of 9T applied along the trigonal axis[11, 12]. The fate of the three-dimensional electron gas beyond this field, invoked years ago from a theoretical point of view[13] has been barely explored experimentally in spite of a number of high-field studies[14, 15]. A recent study of pure bismuth detected unexpected transport anomalies in this regime[16] indicating unknown many-body effects. The decrease in carrier density induced by Sb doping should push the quantum limit to even lower and more accessible fields. A last motivation is provided by the Dirac fermions, which are expected to become massless with the closing of the L-point gap at x=0.04[17, 18]. In this Letter, we present a study of electric and thermoelectric transport in semimetallic $Bi_{0.96}Sb_{0.04}$ extended to low temperatures (0.15 K) and high magnetic field (28 T). In zero magnetic field, we find two hallmarks of a Fermi-liquid behavior namely, a T^2 resistivity and a T-linear Seebeck coefficient. The magnitude of both point to a remarkably small Fermi temperature. The electronic mobility, while significantly reduced compared to pure bismuth, remains high in this alloy. Then we present quantum oscillations of transport properties (and in particular the Nernst coefficient), whose period quantifies the size of the Fermi surface. The quantum limit, for a field along trigonal occurs at 3 T, i.e. three times lower than in pure bismuth. Finally, we resolve anomalies in all transport properties occurring at a field of 6 T. This field scale, which cannot be attributed to the crossing of the Fermi level by a known Landau level is reminiscent of (and different in position with) the case of pure bismuth [16]. Its explanation appears to be beyond the one-particle picture.

Single crystals of $Bi_{1-x}Sb_x$ were prepared using a traveling heater method as detailed in ref. [7]. The nominal concentration of antimony in the single crystalline samples studied in this work was 4 percent. Assuming that the lattice parameter is a linear function of x and by measuring it in a small piece cut from the sample by powder diffractometry, we found an antimony concentration of $x = 0.037$. The longitudinal electrical and thermal conductivity, as well as Hall, Seebeck and Nernst coefficients of the system were measured using a standard 6-wire method with two thermometers and one heater in a 12 T superconducting magnet for two different orientations of magnetic field. The results were complemented by a set of measurements for the trigonal configuration with a 28 T resistive magnet.

Fig. 1 summarizes the transport properties of the system in the zero-field limit. As seen in panel *a*, resistivity is a quadratic function of temperature ($\rho = \rho_0 + AT^2$), the expected behavior of a Landau Fermi liquid. The magnitude of the A coefficient ($33 n\Omega cm K^{-2}$ in the $T < 5K$ range) is almost three times larger

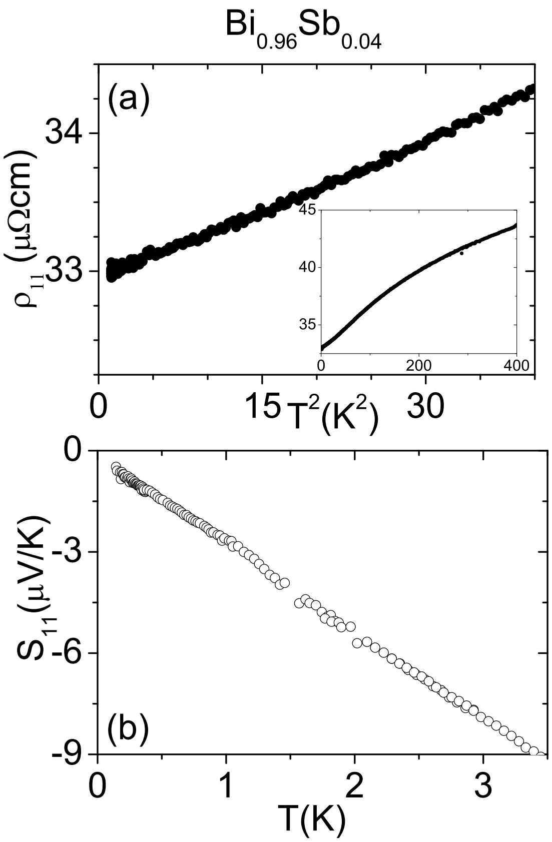

FIG. 1: (a) The zero-field resistivity $Bi_{0.96}Sb_{0.04}$ as a function of T^2 for a current along the binary axis. The inset shows the data over a wider temperature range. (b)The temperature-dependence of the Seebeck coefficient at low temperatures for a temperature gradient along the binary axis.

than in pure bismuth($12n\Omega cmK^{-2}$)[19, 20]. The enhanced A is a natural consequence of the reduction in the Fermi temperature. It is instructive to contrast the magnitude of A (remarkably large for these light-electron semimetals) with the modest magnitude of the electronic specific heat, which has been reported to be as low as $\gamma = 8.5\mu Jmol^{-1}K^{-1}$in pure bismuth[21]. Thus, the Kadowaki-Woods (KW) ratio ($\frac{A}{\gamma^2}$[22]) in semimetallic bismuth is five orders of magnitude larger than in high-carrier density metals (i.e. those with roughly one itinerant electron per formula unit). Theoretical examinations of the KW ratio had already concluded that this ratio should increase as the Fermi surface decreases in size[23, 24]. Its exceptionally large value in bismuth, however, had hitherto escaped attention.

As seen in the panel b of the same figure, the Seebeck coefficient is negative and quasi-linear in temperature below 3 K. Our data smoothly join the reported high-temperature behavior[7]. In contrast with pure bismuth, no remarkable structure at low temperature emerges and a large slope ($\frac{S}{T} \simeq -2.7\mu VK^{-2}$), the expected consequence of the small Fermi temperature can be easily extracted. We note that the dimensionless ratio of linear thermopower to linear specific heat ($q = \frac{S}{T}\frac{eN_{Av}}{\gamma}$), where e is the electron charge and N_{Av} the Avogadro number) is more than four orders of magnitude larger than unity, the typical ratio found in metals with conventional carrier density[25]. Since q is expected to inversely scale with carrier density[25], this is not surprising. It is instructive to compare the low-temperature thermoelectric responses of $Bi_{0.96}Sb_{0.04}$ and Bi. In pure bismuth[26], it is non-monotonous and very small below 1K indicating that contributions by electrons and holes to thermopower are comparable and cancel out at very low temperatures. On the other hand, the frankly negative and T-linear Seebeck coefficient in $Bi_{0.96}Sb_{0.04}$ implies the domination of electron-like carriers. Since the system remains compensated the contraction of the volume of the electron and hole pockets should be strictly equal. Therefore, this predominance cannot be simply explained by the difference in the evolution of the hole and electron Fermi energies with Sb doping. On the other hand, close to x=0.04, the energy spectrum of the electron pocket, which is only partly linear in momentum in the case of pure bismuth becomes strictly linear. Thus, the negative sign of the thermopower reflects the enhanced thermoelectric response of Dirac fermions compared to conventional quasi-particles.

We also measured the thermal conductivity of the sample in zero field (not shown) and found that it is dominated by lattice thermal conductivity as in pure bismuth with an almost undetectable electron contribution[27].

To probe the Fermi surface quantitatively, we studied the quantum oscillations of various transport properties. As seen in Fig.2, in presence of a quantizing magnetic field along the trigonal, both resistivity and the Hall effect show visible oscillations. Panel c of the same figure, a semi logarithmic plot of resistivity *vs.* inverse of the magnetic field, reveals an oscillation period of 0.45 T^{-1}, three times larger than in pure bismuth ($0.15T^{-1}$)[11, 12]. This means that the equatorial cross section of the hole ellipsoid has become three times smaller. The quantum limit, the passage to the $n = 0$ Landau level, occurs at field of about 3T. Note also the additional anomaly in both ρ_{xx} and ρ_{xy} at a yet higher field ($\sim 6T$).

As seen in the main panel of Fig. 3, quantum oscillations of the Nernst response are easily detectable. Their large amplitude is reminiscent of (but less pronounced than) the case of pure bismuth[12]. The period of these oscillations matches the period of Shubnikov-de Haas oscillations of Fig.2. Each Nernst maximum is concomitant with a resistivity minimum. One remarkable feature is the emergence of new peaks at the lowest temperature linked to the large Zeeman splitting. In bismuth for a field along trigonal, the Zeeman energy, E_Z, of holes is such that $E_Z = 2.17\hbar\omega_c$ [11]. In other words, the Zeeman splitting is so large that the field corresponding to the 0^+ peak is *lower* than the one associated with 2^-. This was detected in both resistivity[11] and Nernst[12] data. Thus, the occurrence of the same feature in our data on $Bi_{0.96}Sb_{0.04}$ indicates that here also $E_Z > 2\hbar\omega_c$.

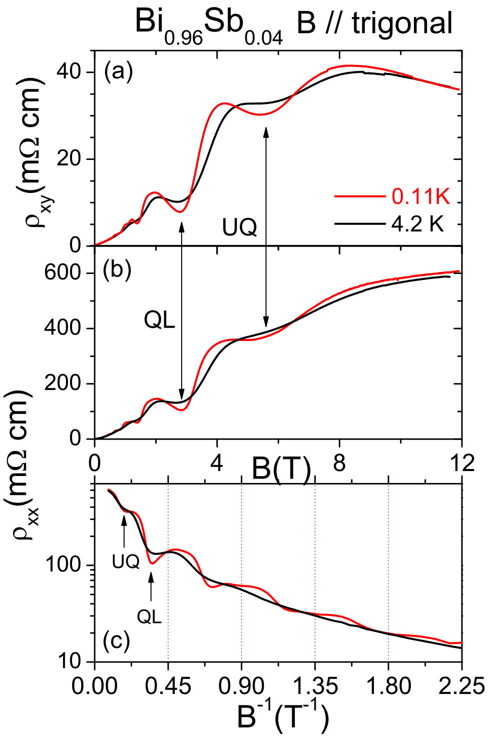

FIG. 2: The Hall(a) and the longitudinal resistivity (b) as a function of magnetic field at two different temperatures. QL marks the quantum limit anomaly. Beyond this limit (i.e. in the ultraquantum regime), another anomaly is visible and marked as UQ. (c) presents a semi-log plot of resistivity as a function of B^{-1}. Quantum oscillations are visible.

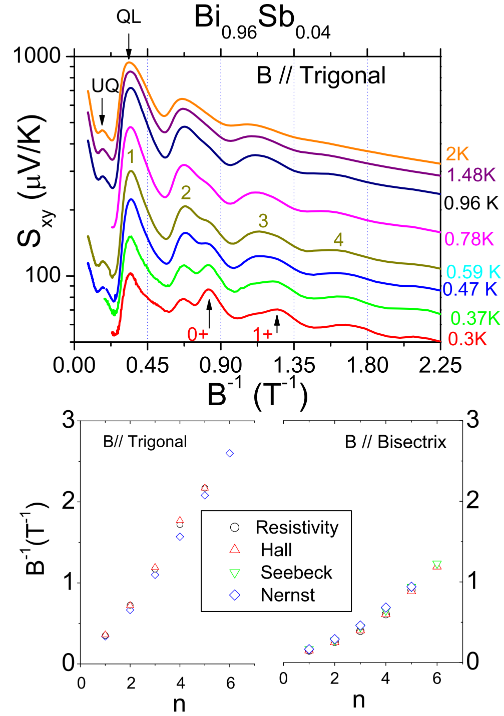

FIG. 3: Upper Panel: Nernst signal as a function of inverse of the magnetic field. Numbers identify peaks associated with various Landau levels. Note the gradual emergence of new peaks due to Zeeman splitting at lower temperatures (See text). The lower panels present the position of identified landau levels for two different field orientations.

System	$P_3^h(T^{-1})$	$P_1^h(T^{-1})$	FS Vol. $(T^{3/2})$
Bi	0.157	0.045	30.0
$Bi_{0.96}Sb_{0.04}$	0.5	0.3	3.64

TABLE I: Period of the quantum oscillations for a field along the trigonal axis, P_3^h, and perpendicular to it, P_1^h, together with the calculated size of the Fermi surface in Bi[29] and in $Bi_{0.96}Sb_{0.04}$. The values correspond to the low-field limit. The Fermi surface volume is calculated as $\frac{1}{P_3^h\sqrt{P_1^h}}$.

As the system cools, the 0^+ anomaly gradually dominates the 2^- peak. We note that this temperature evolution is more radical here than in the case of pure bismuth [12].

The period of quantum oscillations varies as a function of magnetic field. This can be seen in the lower panels of Fig.3 which presents the B^{-1} position of successive Landau levels for both orientations of magnetic field. If the period was constant, the data would fall on a straight line. The upward curvature is reminiscent of the case of pure bismuth[11] and is a signature of a field-induced modification of the carrier density and Fermi surface volume. According to a picture proposed many years ago[28], charge neutrality in this compensated system implies a continuous adjustment in carrier density of both holes and electrons. This leads to a steady increase in the size of the Fermi surface, in particular in the vicinity of the quantum limit. As seen in the lower panels, the upward curvature is much stronger for a field along the bisectrix, which was also the case in pure bismuth[28].

Table 1 compares the period of quantum oscillations in Bi (according to one authoritative studiy[29]) with what is found here for $Bi_{0.96}Sb_{0.04}$ at the low field. For each field orientation, the frequency of oscillations directly yields the projected area of the Fermi surface. Hence, the volume of the hole ellipsoid can be unambiguously determined. It is smaller by a factor of 8 in the alloy. Even though the electron pockets have remained invisible, their overall volume is expected to contract identically. Indeed, the system is expected to remain compensated during the smooth evolution towards the insulator. Thus, we conclude that the carrier density for both electrons and holes in $Bi_{0.96}Sb_{0.04}$ is $4\times10^{16}cm^{-3}$. This is in fair agreement with the estimation by Brandt and co-workers[6]. It is remarkable to find that a Fermi liquid behavior persists at such a low level of carrier concentration. A residual resistivity of 32 $\mu\Omega cm$ for such carrier density (assuming an equal mobility for electrons and holes) would imply a mobility of $2.4\times10^6 cm^2V^{-1}s^{-1}$, significantly lower than bismuth[19], but remarkably high for an alloy .

In order to investigate the transport properties of the system deep in the ultraquantum regime, the $Bi_{0.96}Sb_{0.04}$ crystal was put in a 28 T resistive magnet of Grenoble

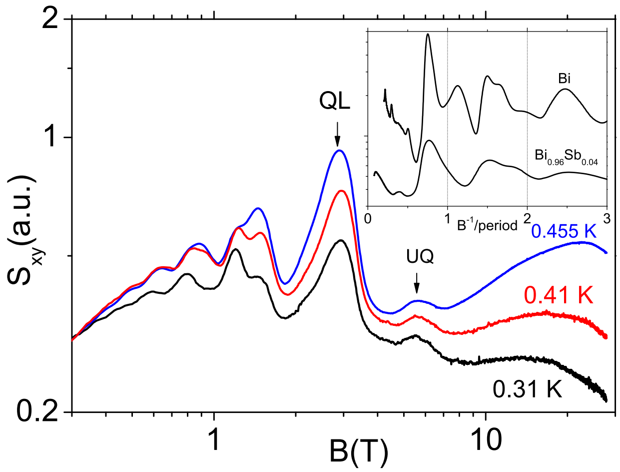

FIG. 4: Nernst data obtained for $Bi_{0.96}Sb_{0.04}$ in a high-field (28T) resistive magnet. The insert compares the alloy with pure bismuth. The 0.45K data and the 0.85K data for Bi[16] is plotted as a function of B^{-1} normalized to the period of oscillations in each case (See text).

High Magnetic Field Lab with a set-up designed for high-resolution thermoelectric measurements in a top-loading dilution refrigerator. The results are presented in Fig.4. As seen in the figure, in addition to the ultraquantum anomaly at 6 T, the data presents a very broad maximum at $\sim$ 18 T. In contrast to the 6T anomaly, the field position of the latter feature evolves with cooling and one cannot firmly identify a zero-temperature field scale.

The inset of the figure compares the Nernst anomalies in bismuth[16] and in $Bi_{0.96}Sb_{0.04}$. The horizontal axis is B^{-1} normalized by the oscillation period in each system (0.15 T^{-1} in the pure case and 0.45 T^{-1} in the alloy). As seen in the figure, in both cases the most prominent peak among the Nernst anomalies occurs at the quantum limit (9T in bismuth and 3T in the alloy). Note also the broadening of the Nernst anomalies in the alloy. As for the ultraquantum regime, as seen in the figure, three sharp anomalies were resolved in bismuth[16]. They occurred at fields corresponding to 3/2, 5/2 and 7/2 times the quantum limit. Here, in $Bi_{0.96}Sb_{0.04}$, we resolve at least one ultraquantum anomaly at twice the quantum limit. We recall that this field scale has very visible signatures in charge transport (See Fig. 2).

Can this anomaly be caused by the electron pockets? Since the latter remain undetected, this question cannot be answered with certainty. However, as seen in Fig. 2 the sign of the jump at 6 T in the Hall resistivity is the same as the 3T anomaly: It is *positive*. A similar feature was seen in the Seebeck data. Both these suggest that this anomaly is linked to the hole-like carriers. In the case of pure bismuth, the electron pockets, which are elusive in transport measurements, dominate the magnetization response and torque magnetometry has emerged as a powerful probe of the electron pockets across the quantum limit[30, 31]. Future angular torque magnetometry studies should shed more light on the origin of the ultraquantum anomalies detected here.

In summary, we studied the transport properties of $Bi_{0.04}Sb_{0.96}$ across the quantum limit and quantified the carrier density and mobility of this semimetal. Even at such low level of carrier concentration, the zero-field ground state is a Fermi liquid. In the extreme quantum limit, at least one anomaly possibly emanating from unknown many-body effects was detected. We thank G. Lapertot for precious technical assistance. This work was supported by the Agence Nationale de la Recherche.

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